

[54] GAS MIXTURE FOR GLOW DISCHARGE DEVICE

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[*] Notice: The portion of the term of this patent subsequent to May 27, 1992, has been disclaimed.

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[21] Appl. No.: 567,793

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 412,576, Nov. 5, 1973, Pat. No. 3,904,915, which is a continuation-in-part of Ser. No. 279,875, Aug. 11, 1972, Pat. No. 3,886,393.

[52] U.S. Cl. 313/226; 313/518; 313/519; 315/169 TV

[51] Int. Cl.² H01J 17/20; H01J 17/48; H01J 63/04; H05B 33/10

[58] Field of Search 313/185, 223, 224, 485, 313/383, 226, 514-521; 315/169 R, 169 TV

[56] References Cited

UNITED STATES PATENTS

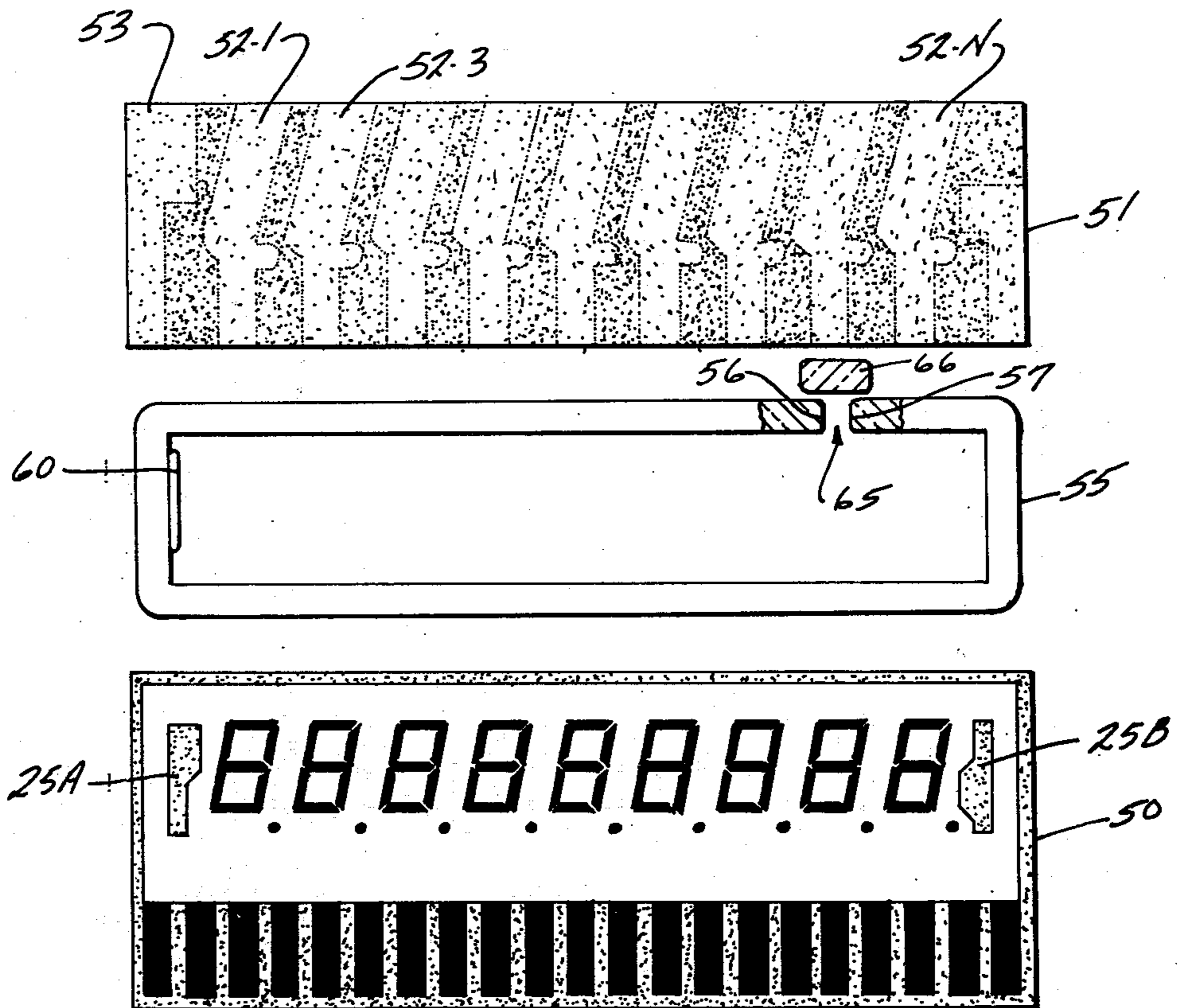
2,714,682	8/1955	Meister et al.	313/185 X
3,886,393	5/1975	Hinson	313/223
3,904,915	9/1975	Hinson	313/485

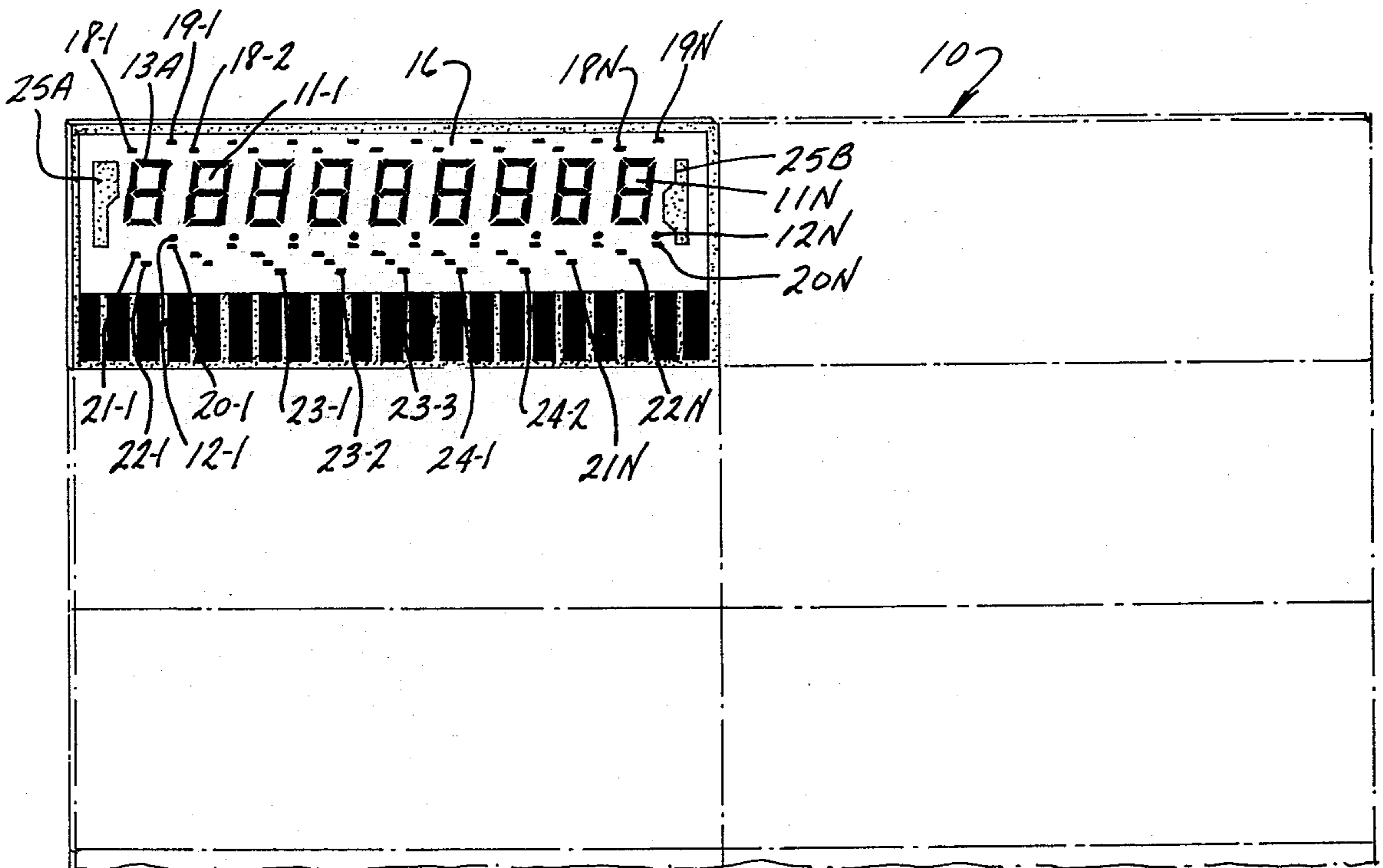
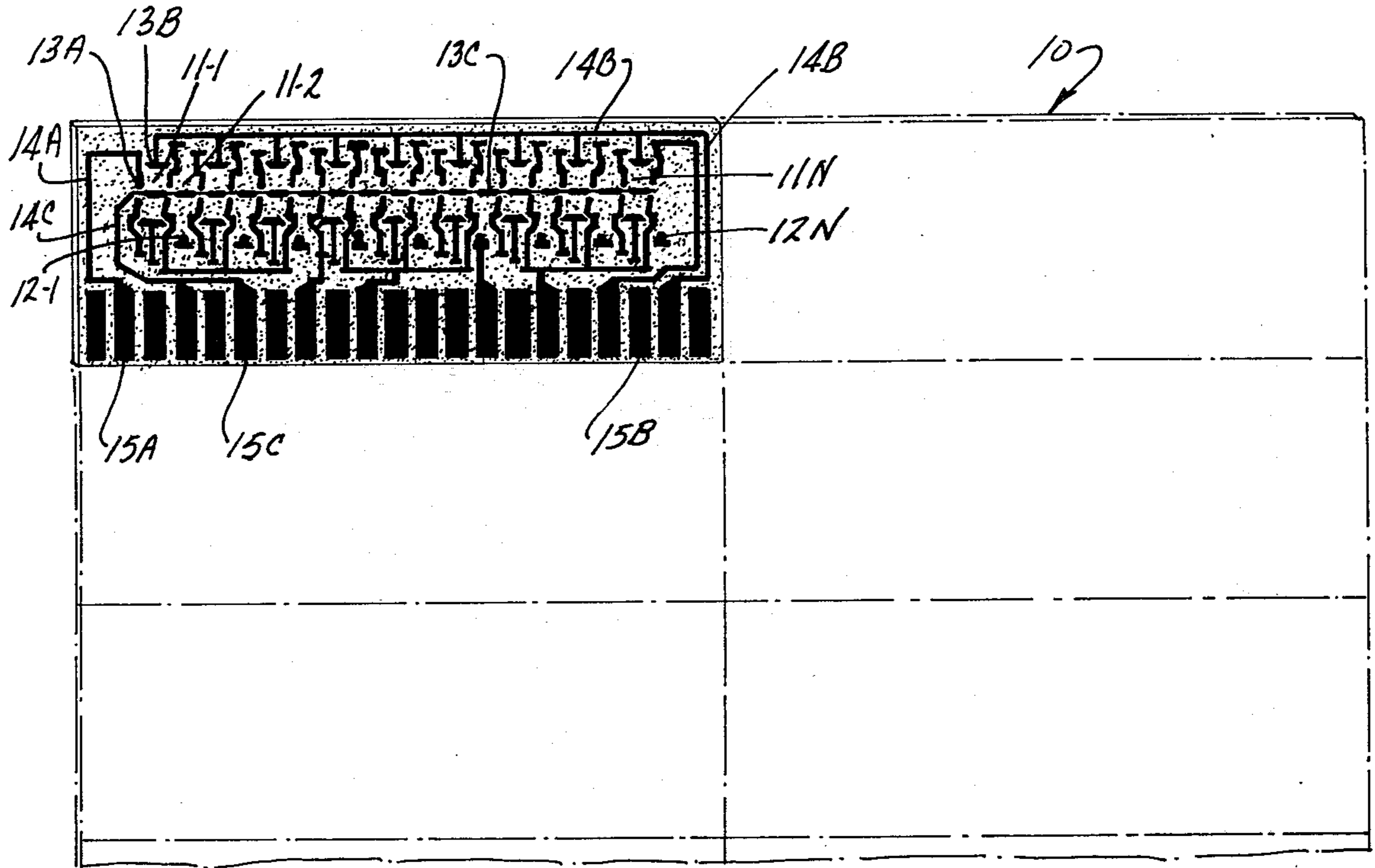
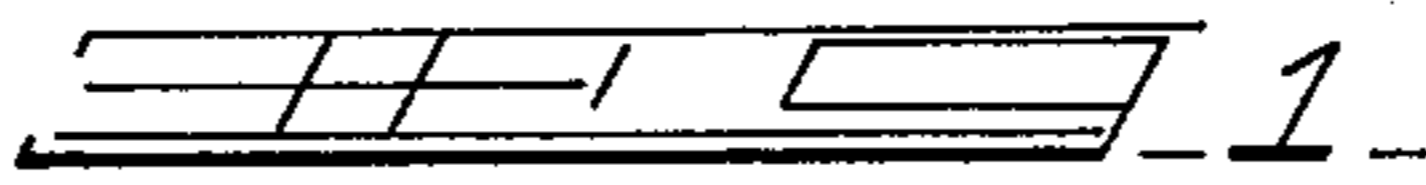
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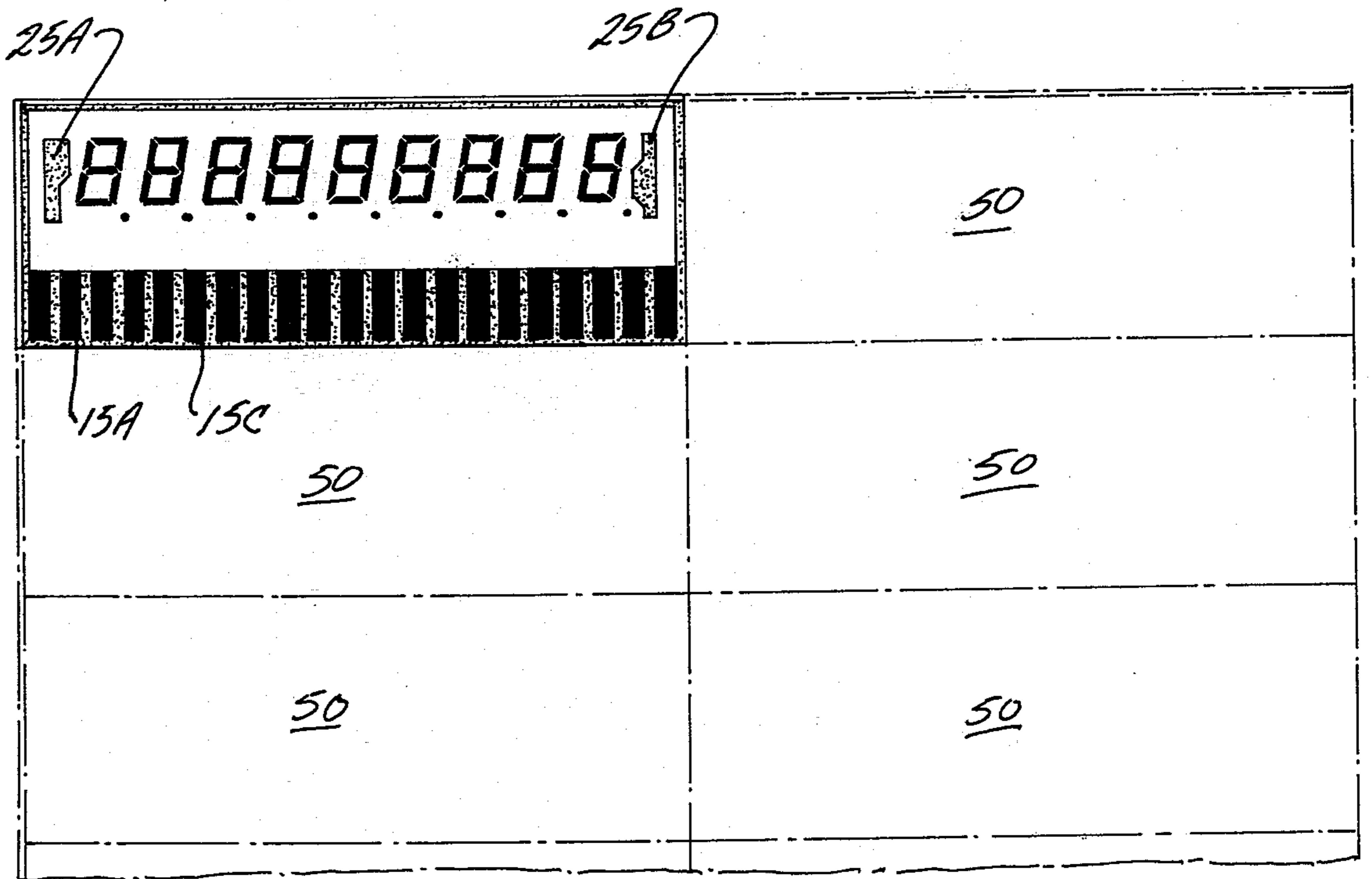
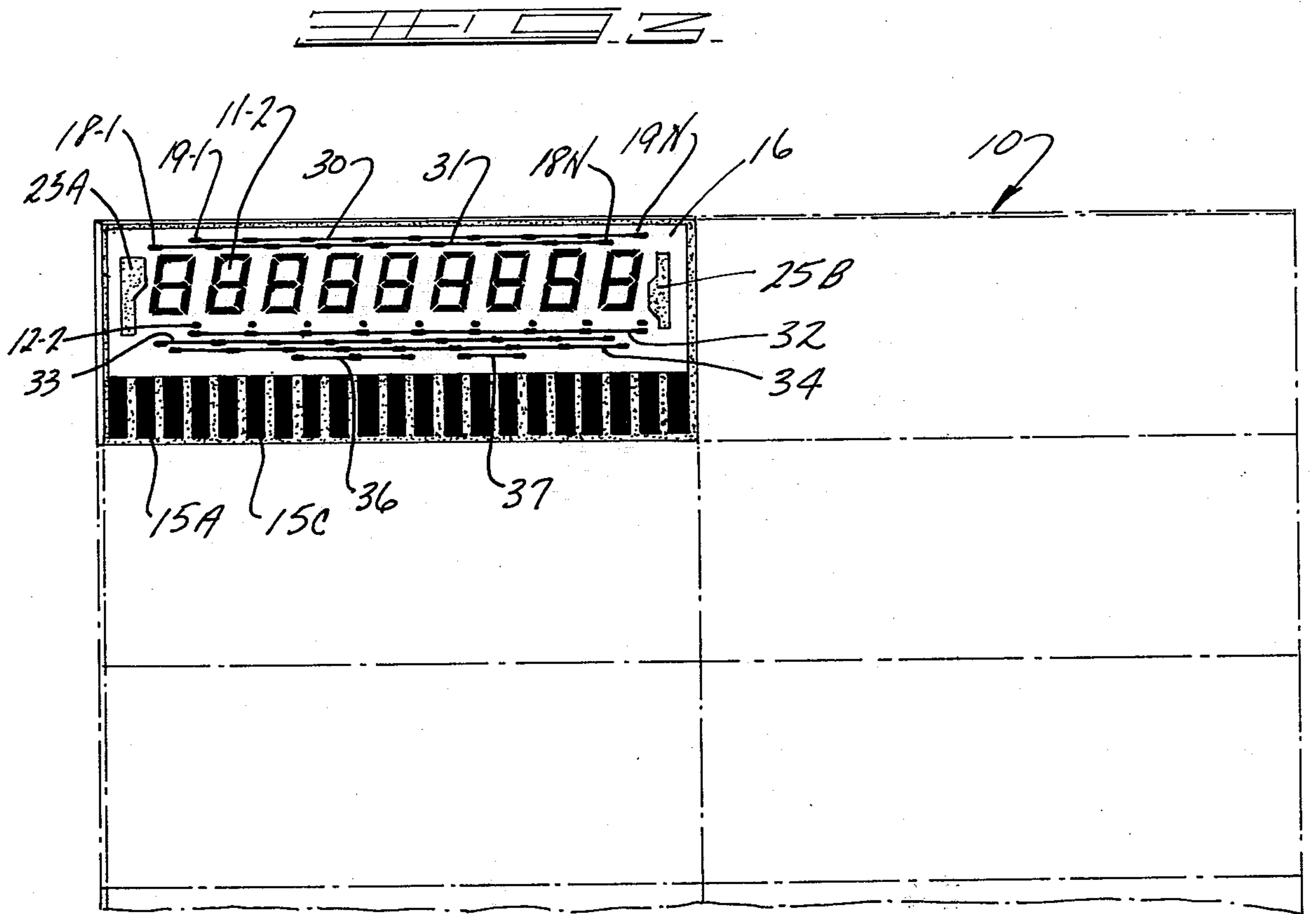
[57] ABSTRACT

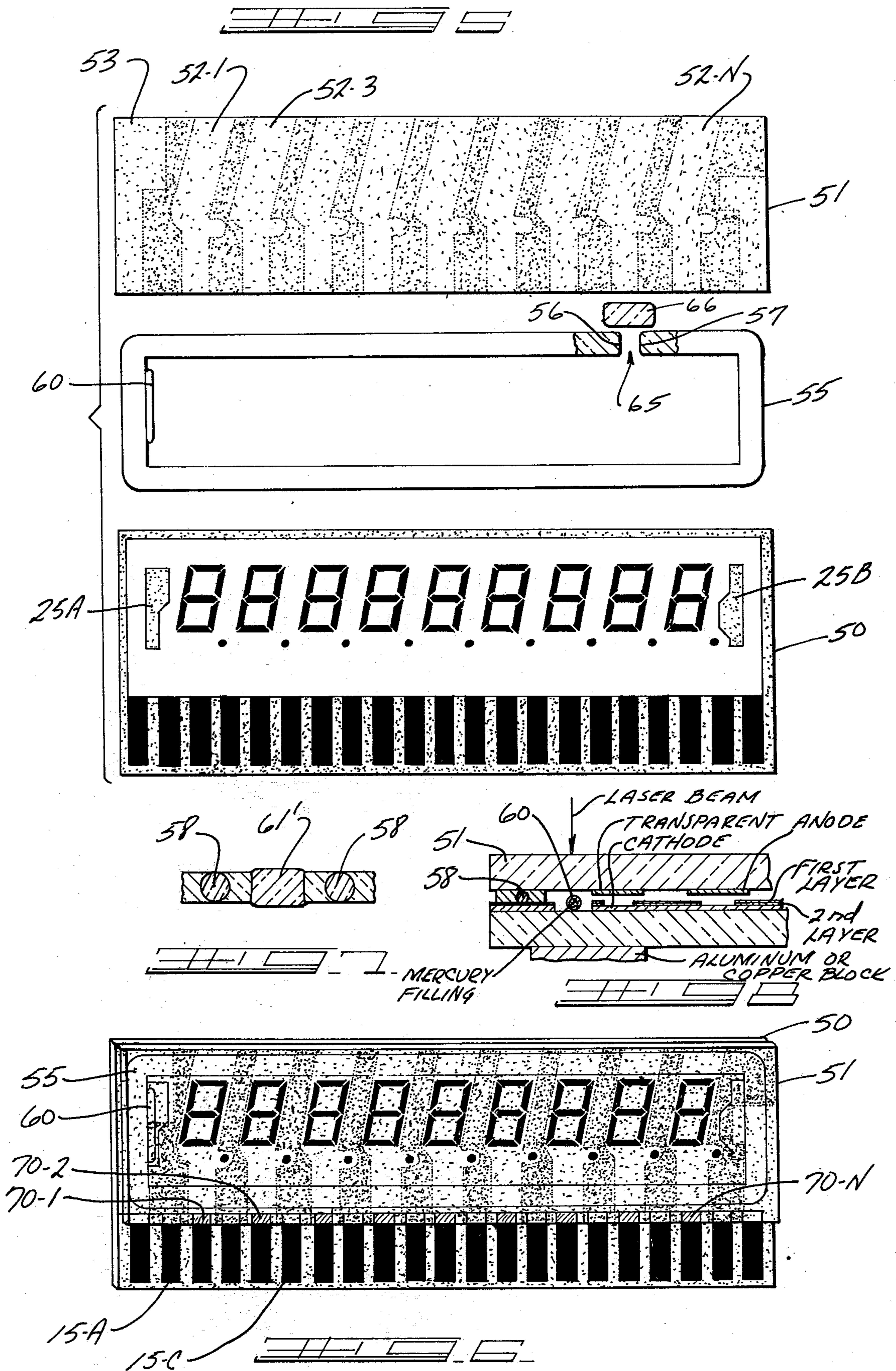
There is disclosed a glow discharge device gas mixture consisting essentially of about 20 to 35 percent atoms of argon and about 80 to 65 percent atoms of a xenon-based composition. The mixture is especially beneficial for use in a color phosphor, direct current (dc) gas discharge device because the mixture substantially lowers device operating currents while providing phosphor stimulation. The xenon-based composition consists essentially of about 95 to 100 percent atoms of xenon and about 5 to 0 percent atoms of another component, particularly one or more selected from neon, krypton, nitrogen, helium, and mercury.

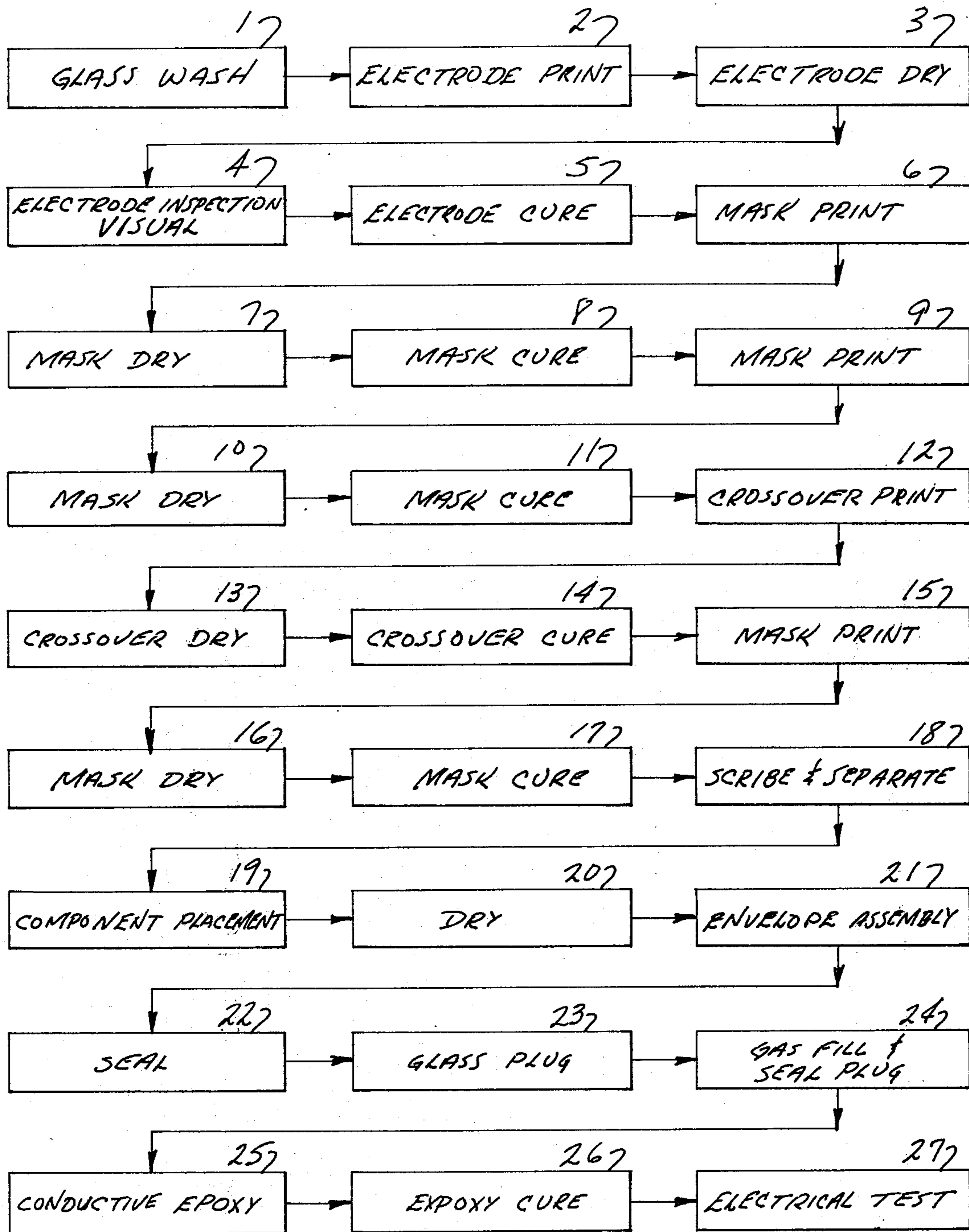
8 Claims, 9 Drawing Figures











PROCESS FLOW CHART
NUMBERS REFER TO PROCESS STEPS



GAS MIXTURE FOR GLOW DISCHARGE DEVICE**RELATED APPLICATIONS**

This is a continuation-in-part of copending U.S. Pat. application Ser. No. 412,576 filed Nov. 5, 1973, now U.S. Pat. No. 3,904,915 which is a continuation-in-part of copending U.S. Pat. application Ser. No. 279,875, filed Aug. 11, 1972, now U.S. Pat. No. 3,886,393.

BACKGROUND OF THE INVENTION

This invention relates to glow discharge devices, especially cathode-anode gas discharge devices operated by direct current and which are capable of producing a visual display or representation of data such as numerals, letters, radar displays, aircraft displays, binary words, educational displays, etc.

Gas discharge display devices of the type contemplated herein are well known in the prior art. Examples of such devices are disclosed in U.S. Pat. Nos. 2,142,106; 3,237,040; 3,497,751; 3,260,880; 3,720,452; and 3,725,713, all of which are incorporated herein by reference.

Such devices comprise an anode and a cathode, typically in direct contact with an ionizable gas mixture. Electrical energy such as a direct current is applied to the electrodes so as to effect a glow discharge in the ionizable gas mixture between the anode and the cathode.

In the construction of the device, a continuous volume of ionizable gas is confined between opposing cross conductor arrays typically forming matrix elements. The cross conductor arrays may be orthogonally related (but any other configuration of conductor arrays may be used) to define a plurality of opposed pairs of glow discharge sites. Thus, for a conductors matrix having H rows of cathodes and C columns of anodes, the number of glow discharge sites will be H times C.

In addition to the matrix configuration, the cathode-anode conductor arrays may be shaped otherwise. Accordingly, while one conductor arrangement is of the crossed grid type as discussed herein, it is likewise apparent that where a maximal variety of two dimensional display patterns is not necessary, as where specific standardized visual shapes (e.g., numerals, letters, words, etc.) are to be formed and image resolution is not critical, the anodes and cathodes may be shaped accordingly, i.e. a so-called segmented display.

Typically, both the anode and cathode are immersed in or otherwise in direct contact with the ionizable gas mixture. However, it is also feasible to have a gas discharge device wherein some of the conductive or electrode members are in direct contact with the gaseous medium and the remaining electrode members are appropriately insulated from such gas by a dielectric or other means.

THE INVENTION

This invention will be described with particular reference to a so-called segmented character, direct current, glow discharge device. However, other electrode or conductor array configurations, i.e. matrix type, are contemplated.

Gas discharge display devices of the character disclosed herein are well known in the prior art. In such devices individual glass substrates and/or ceramic substrates are provided upon which the conductor runs are printed and then the dielectric masks are printed over

the conductor runs and in the openings in the conductor runs for the cathode electrodes, the cathode materials which interface with the gas discharge medium are printed thereon and all of these being subsequently fired and cured. Such devices are subsequently assembled usually by the use of a gas filling tubulation but in some cases tubulationless devices have been fabricated in which final hermetic seal of two spaced apart substrates is accomplished by utilization of an unfused sealing frame, evacuating the entire unit and back filling with an elevated temperature and then heating the assembled parts spaced between the electrode elements while retaining the gas in the assembly until the glass parts have been softened to a sealing temperature to result in a fusion sealing of the frame element and thereby final assembly of the device.

In U.S. Pat. No. 2,142,106 issued to Boswan, a gaseous discharge display device having small glass discs carrying shaped cathode elements and individual anode elements are stacked in a disc with the interstices between the discs sealed in a manner around the periphery to prevent electrode interference between each other, a small aperture being left at one point in the periphery by leaving out the sealing operation at this point to provide communication with the main gas chamber formed by an overall glass envelope or bulb. In the Boswan patent, the bulb is subsequently exhausted and filled with the gas at a proper pressure, the exhausting and back filling processes extending through and communicating through the aperture to the individual gas chambers formed in the spaced disc and the aperture then is filled with a suitable sealing material which permits the gas to permeate during the exhausting and filling operation. Thereafter this individual seal element or plug is sealed by heating means of electronic bombardment or other sealing means.

In one embodiment of the present invention, there is provided a direct and distinct improvement over the sealing technique disclosed in the Boswan patent in that the present invention adapts a portion of that technique of the Boswan patent to incorporate spaced elements in the sealant and extends some to batch processing of thousands of individual discrete gaseous discharge panel elements in a manner and fashion not heretofore available, with yield factors significantly greater than those of the prior art. A small opening or space between the ends of the rod is provided. Large numbers of the device may be stacked in trays and back filling with the desired gas composition of this invention of large numbers of individual devices in a single operation.

In a further preferred embodiment of this invention, instead of using a ceramic substrate, simple, inexpensive glass substrates are used. The conductor elements forming the cathode electrodes which interface with the gas medium are printed first and cured. The portions of the conductive printing which are actual anode elements, may be nickel plated with electrodeless nickel to reduce sputtering. During the nickel plating, the conductor portion to the exterior of the device are shielded. The reason for shielding is that the seal area must be sintered and not porous.

In the sealing operation, it has also been found that the use of screened on sealing materials in an unfused state permits the incorporation of the spaced therein and the forming of the seal under non-vacuum conditions permits such seals to be made, particularly when the glass gob sealing technique is utilized.

Then, after the gas filling has been introduced to the devices, the devices are heated by Calarod heaters inside the chamber so as to effect a melting of small glass sealing gobs in the fill ports or openings described earlier herein.

In accordance with this invention, there is provided a glow discharge device gaseous mixture consisting essentially of about 20 to 35 percent atoms of argon and about 80 to 65 atoms of a xenon-based composition. The mixture is especially beneficial for use in a color phosphor, direct current (dc) gas discharge device (of the segmented or matrix types disclosed herein), because the mixture substantially lowers device operating currents while providing phosphor stimulation. The xenon-based composition consists essentially of about 95 to 100 percent atoms of xenon and about 5 to 0 percent atoms of another component, particularly one or more selected from neon, krypton, nitrogen, helium, and mercury.

The gas mixtures of this invention are generally maintained at low pressures within the device, e.g. less than 250 Torr, preferably less than 100 Torr, typically less than 50 Torr.

DESCRIPTION OF THE DRAWINGS

The above and other objects, advantages and features of the invention will become more apparent from the following description taken in conjunction with the accompanying drawings which represent some of the best embodiments contemplated by the inventor in the practice of the invention.

FIG. 1 illustrates a glass substrate upon which a first conductive pattern has been printed, one such pattern being shown in the top left hand corner thereof with the dash lines indicating the positions of a large number of other such patterns not shown in this drawing for purposes of clarity of explanation.

FIG. 2 illustrates the glass plate of FIG. 1 upon which has been printed the first dielectric mask (a black colored dielectric but shown white in FIG. 2),

FIG. 3 is the plate shown in FIG. 2 having the crossover conductors printed on the mask of FIG. 2 interconnecting the different elements shown, it being understood that a similar printing has occurred with respect to the other substrate elements shown in FIG. 3,

In FIG. 4, a further dielectric printing has been accomplished over the crossover elements shown in FIG. 3,

FIG. 5 is an exploded view showing the sequence of assembly of the different components into a device ready for gass fill and seal operations,

FIG. 6 is a top plan view of a completely assembled device,

FIG. 7 is an enlarged sectional view showing the placement of the gob of sealing glass bridging the gap on the fused seal frame,

FIG. 8 shows the mercury capsule in position with a laser beam directed thereto for fracturing same,

FIG. 9 is a process flow chart showing the individual printing and curing operations utilized in the manufacture of the devices.

DETAILED DESCRIPTION

Referring now to FIGS. 1-8 in conjunction with FIG. 9, FIG. 1 shows a glass plate 10 which, in a specific example, may be ten inches by twelve inches single strength glass, has printed thereon individual cathode electrode patterns 11-1, 11-2, 11-N and cathode period

elements 12-1, 12-N. Each cathode pattern constitutes a digit position, the illustrated embodiment being for a nine digit numeric display (n-9). It will be appreciated that the invention is equally applicable to alphanumeric segmentation as well as crosspoint matrix display. These elements have cathode electrode segments 13A, 13B etc. which, in the embodiment of this invention, constitute the cathode electrode elements defining the glow discharge portions of the display. It will be noted that certain ones of these cathode segments 13A, leading to a conductor pad 15-A. In the embodiment of this invention to be described herein, each of the corresponding segments 13-A in all of the digit positions 11-1, 11-2 . . . 11-N, are interconnected electrically, some of which are directly interconnected in the initial electrode printing shown in FIG. 1. For example, the center bar segment 13-C is shown as being an interconnected horizontal segment electrode and by conductor portion 14-C to a pad 15-C. Alternate pads are also printed at this time for subsequent connection to the anode elements to be described later herein. In like manner, the cathode electrode 13-B in digit position 11-1 is interconnected to every cathode segment designated with the numeral B by a conductor portion 14-B and thereby to a pad 15-B.

However, in accordance with the present embodiment, some of the cathode segments are not directly connected to conductors extending to the individual pad elements 15. In the illustrated embodiment, a first dielectric mask element 16 shown in FIG. 2 is printed over the conductor segments leaving openings or vias 18-1, 18-2, 18-N and 19-1, 19-2, 19-N and 20-1, 20-N, 21-1, 21-N and 22-1, through 22-N, all of which are in registry with an underlying conductor portions or areas. These vias are simply opening or spaces left vacant in the dielectric mask or layer 16. In addition to the vias or openings left for crossover connections, to noted that the individual cathode segments 13-A, 13-B, etc. and the periods therefor 12-1 . . . 12-N, are left open. As has been described earlier, no further conductive material is applied to these cathode elements because they have been cured at a higher temperature to thereby anneal and/or provide smooth surfaces for the discharge per se. However, these cathode segments may preferably be plated with electrodeless nickel in a conventional plating batch or process, before or after the dielectric mask has been applied, care being taken to assure that at least the conductors in the seal area are shielded from the plating operation which assures a good seal being made. In reference to FIG. 9, this plating operation may be done in place of steps 6-8 in which case the mask print, dry and cure steps are performed as steps 9-11. Alternatively, the plating of the cathode segments (the conductor portions in contact with the gas) may be done through the cathode openings in the mask. The crossover vias, 18-1 . . . 18-N, 19-1 . . . 19-N, 20-1 . . . 20-N and 22-1 . . . 22-N are left open for the purpose of permitting the conductor material which is printed in a manner shown in FIG. 3 to make electrical contact with the conductor elements exposed by the vias. These form the electrical crossover connections shown in the pattern of FIG. 3. It will be appreciated that conductor patterns may be devised so that the printing of such crossovers is eliminated or minimized. It should be understood that while the dielectric mask is shown as white, it is black mask for highlighting the glow discharges at the cathode segments, and that the cathode material is white or silver

colored in appearance and, in fact, is basically a silver in a suitable vehicle. Furthermore, clear or transparent areas of glass have been stippled. Of course the anode glass substrate could be translucent.

In addition to the openings or vias to make the crossover connections and in addition to the opening for permitting the cathode segments to be viewed in direct conductive contact with the gas, a pair of windows 25A and 25B are provided so that the glass substrate 10 is directly viewable through these openings 24 and 25. These openings are for the purpose to be described more fully hereinafter.

Not shown in FIGS. 1 or 2 are conventional registration marks, the registration marks simply being marks which are printed in dielectric material upon the substrate 10 and in any subsequent printing upon the substrate 10 when the dielectric material is printed so as to assure registration thereof. In like manner, in the following page which also follows, further printings of the registration marks are made to assure the proper registrations are achieved. The term printing is used principally to encompass stencil screen printing etc., but other forms of printing may be used.

As shown in FIG. 3 the crossover interconnecting via 19-1 through via 19-N is designated with the numeral 30 and the crossovers connecting the vias 18-1 . . . 18-N are designated 31. In like manner, crossover conductor means 32, 33 and 34 are conductor printings upon the dielectric. The printing operations are simply screening or otherwise applying the conductive material directly upon the dielectric surfaces of the substrate with the conductive material entering the vias and making the electrical contacts with the conductor previously printed. It will also be noted that a pair of crossovers 36 and 37 have also been printed upon the conductor solely for the purpose of making the crossover connections between the conductor elements as shown.

It will be noted that the conductive cathode segments for each of the digit positions remains exposed and these elements are, in effect, continuing to receive the temperature treatments (albeit at lower temperatures) for the curing of the dielectric layer 16 and the individual crossover layers as shown.

In a final printing operation, the final dielectric layer is applied over the crossover, the windows 25A and 25B being maintained. The purpose of this final printing is, as is well known, to avoid any glowing of conductor areas or portions which is it is not desired to glow.

Referring now to FIG. 9, it should be noted that an important step in the process just described in the fabrication of the back substrate is that the electrodes which form the cathode segments for the display have been printed in an initial printing operation and that the cathode portions have been plated with electrodeless nickel without adversely affecting the conducting properties of the different conductor elements used in providing exterior connections for the device. As shown in FIG. 9, the initial mask is printed in a two step operation of, first, printing the mask a first time, drying the mask and then curing the mask. A second mask printing, drying and curing operation is effected but it will be appreciated that these may be done in a single step. In some cases, the mask may be fabricated as a film and transferred to the substrate. However, it is important to assure that the mask is of a sufficient thickness that the gap adjacent cathode segments is separated by a physical barrier of dielectric material. Thus, this second step

is an important assurance that the dielectric between the ends of individual cathode segments is high enough to provide a barrier which avoids or minimizes shorting between nearby cathode segments.

The crossover printing is done with the same conductive material as is used in the first printing operation of conductive material and it will be noted that in each case, the conductive material is dried and then cured at higher temperatures. This material is a frit based thick film paste primarily of silver. The third mask printing operation, while it could have been limited to printing simply over the crossovers, was, in effect, a full printing since this further assured a sufficient barrier between the individual cathode segments on the substrate. Thus, in addition to being able to print, dry and cure the cathode electrodes at a high enough temperature (a typical conveyor oven being about 50 ft. long, one foot per minute, there being about 15 heat zones with a maximum temperature of 1100° C) as to assure a good, clean, smooth silver surface for the cathode electrode, printing the cathode electrodes in a first printing step permits a good plating operation to be performed and to mask areas of sufficient barriers between the individual cathode segments as to reduce the possibility of conductive connections between the individual cathode elements due to the sputtering, etc. and thereby enhance the active life of the device.

As illustrated at box 18 of FIG. 9, the device is scribed along the dash-dot lines and separated to provide individual back substrates illustrated in FIG. 5 as element 50. Element 50 is identical to the different element 50 shown in FIG. 4.

Referring now to FIG. 5, the back substrate now designated as element 50, is identical to the back substrate component shown in FIG. 4. Also shown in FIG. 5 is an anode substrate 51 having printed thereon individual anode elements 52-1, 52-2, 52-N, there being one such anode electrode element for each digit position and adapted to overlie the individual cathode segments and the cathode period element 12-1 at a given digit position. The anode conductors are transparent tin oxide which are printed and fired on a single strength glass substrate 53. It will be appreciated that the printing and firing of these conductors may be done in a batch process, very much like the printing of the back substrate with cathode elements. The use of tin oxide as a transparent anode element is conventional in the art and is not described in detail herein except to say that the process of printing same with large numbers of devices on a thin glass substrate is useful for the purpose of batch producing devices.

The top substrate or anode plate 51 is joined to the bottom substrate by means of a screen printed sealing element or member 55 which, in a preferred embodiment, has been shaped so as to have the ends thereof 56 and 57 spaced by about a one-fourth inch to about one-sixteenth inch. The sealing element 55 is screened upon the black dielectric masked element and at the same time small glass spacer beads 58 are likewise temporarily held in position by tacking as by the use of unfused dielectric. Spacer beads 58 and 59 consist of a hard glass composition having a higher softening temperature than the sealing element 55. The seal element 55 is conventional solder glass sealant which has a fusing or seal temperature below the melting point of the glass substrate 10 and spacer beads 58. Beads 58 provide accurate spacing for the discharge gaps.

In addition, a small mercury capsule 60 is held in place in position over window 25A by a white unfused dielectric which is of essentially the same composition as the dielectric forming the mask but which does not have any pigmentation in it. The purpose of using a white unfused dielectric is so that a laser energy which is used to rupture the capsule 60 is not absorbed by the black dielectric to create heat in the black dielectric and thereby destroy the device. It is also for this reason that a pair of windows 25A and 25B is provided.

After the sealing member 55 and spacer beads 58 and mercury capsule 60 have been positioned in the device, the anode plate 51 is positioned over these elements and a weight is applied thereto. The entire assembly is passed through a heating oven to fuse or join the sealing member 55 to anode plate 51 and back substrate plate 50. A glass sealing gob 66 is simply laid in the gap or crvice between back substrate plate 50 and anode plate 51 and constitutes the glass plug illustrated in block 23 of FIG. 9. The resulting device is illustrated in FIG. 6.

The only size criteria of the spacer is that it defines the discharge gap and be a high melting temperature glass and have a fiber softening point below that of seal member 55.

As shown in FIG. 6 alternate ones of contact pads 15 are connected to the cathode electrode on cathode plate 50 and the intervening ones are connected by means of an extruded conductive silver epoxy connectors 70-1, 70-2 as an improvement over prior art metal insert connectors previously used for this purpose. It is important to cure the epoxy at a temperature such that bubbles are not formed. Bubbles tend to cause concentrations of current flow in the tin oxidized coatings and thereby impair or destroy the connection thereto.

As shown in FIG. 8, the mercury giver 60 is a filamentary glass tube (18 mils in outside diameter) which is laser energy transparent. It is positioned between a window 25A and the cathode plate 50 and a transparent portion of the anode plate 51 (which may also be designated as a "window") and held in place for assembly purposes by a white dielectric. The aluminum or copper block serves as a heat sink and should not be highly reflective for safety reasons. Instead of a glass capsule to giver may be any other radiant energy actuable device, such as SAES type 150 giver from the SAES company of Italy. It will be understood that by nickel plating the cathode segments, sputtering of the cathode segments is minimized.

The gas filling is a mixture of xenon and argon, as specified hereinbefore. As is conventional, radioactive Krypton (Krypton 85) may be added to the fill mixture to lower the operating voltage. However, it will be noted that there are two unused contact pads 15 which could be used to operate a keep alive discharge as is also conventional in the art. If desired the top horizontal run of seal member 55 may be located closer to the edge so that upon fusion the seal material of element 55 will be pressed flat as shown in FIG. 8 and the seal plug 66 held in position. The panel assemblies, with glass seal gob 66 in the notch or space and bridging the ends of the seal element 55, the panels are stacked, in stainless trays with the port or space 65 up and the glass gob 66 in place. A high temperature glass shim, not shown, is located between the lower edge of anode plate 51 to maintain the proper relationship between the anode and cathode plates while the heating of seal rod 66 is performed.

Seal element 55 is a bubble-free glass to avoid "worm" holes therein. The glass plugging element or gob 66, placed across the opening or port 65 as shown, has softening point below that of the sealing member 55; a similar glass with a softening point 20° to 30° lower is satisfactory.

The gas process procedure is the evacuation of the system, the introduction of the proper gas at ambient room temperature to the proper pressure, about 120 torr, and the heating of the seal rod so it closes the envelope with the desired gas condition. In the system described above, the cycle is 6 hours with 2,000 devices per cycle. Each chamber can be large enough to handle as many as 5,000 devices. The cycle may be reduced to 1½ hours. After the sealed devices are removed from the gas process system, each one is placed under a laser which is projected through window 25A in the device to crack the capsule and release mercury into the envelope. As is conventional in the art some panel aging time may be performed before releasing the mercury.

One method of eliminating mercury is the use of cathode materials other than the silver or other precious metals previously used in these devices. The materials to be used according to this invention are silicon carbide, nickel boride, molybdenum disilicide, tungsten boride, chromium boride, and a number of other elements of this nature. Although these materials are known to be sputter resistant they could not be used prior to the present invention because they are extremely hard and brittle and could not be rolled into strip form to be used as cathode elements. However, these materials can be obtained in powder form and incorporated into the conductive inks of this invention and printed in accordance with the above-mentioned process.

Also this invention encompasses plating or covering cathode elements with various nickel plating solutions which are extremely resistant to sputtering. One such coating is nickel boride. Nickel itself if printed in a glass frit and fired in air will be oxidized rapidly to a nonconductive and use less nickel oxide. By contrast the nickel boride coating on a standard precious metal or other type cathode substantially eliminates all sputtering and provides a long lasting display device. The embodiments of this invention eliminating use of mercury vapor substantially reduce the cost of producing a display device as well as insure freedom from the well-known health hazards of mercury and mercury vapor. However, other aspects of this invention may be used in conjunction with mercury capsule 66.

It will be appreciated that while a number of modifications have been referred to, others will become apparent to those skilled in the art and it is to be understood that such obvious modifications may be made without departing from the true spirit and scope of the claims appended hereto.

I claim:

1. In a process for operating a cathode glow gas discharge information display device which comprises a matrix of gas discharge cells, each having at least one cathode electrode element having a configuration defining the glow discharge portion of the display, and an ionizable gaseous medium, the improvement which comprises decreasing the device operating currents by operating the device with an ionizable gaseous medium consisting essentially of about 20 to 35 percent atoms of argon and about 80 to 65 percent atoms of a xenon-

based composition, said xenon-based composition consisting essentially of about 95 to 100 percent atoms of xenon and about 5 to 0 percent atoms of another selected component.

2. The process of claim 1 wherein the other component is a member selected from neon, krypton, nitrogen, helium, and mercury.

3. The process of claim 1 wherein the device contains at least one phosphor, with radiation from the gas discharge exciting the phosphor.

4. The invention of claim 1 wherein the device contains at least one phosphor, with radiation from the gas discharge exciting the phosphor.

5. The invention of claim 1 wherein the gaseous medium is at a pressure of 100 Torr or less.

6. In an article of manufacture comprising a cathode glow discharge information display device containing a matrix of gas discharge cells, each having at least one cathode electrode element having a configuration defining the glow discharge portion of the display, and an ionizable gaseous medium, the improvement wherein the gaseous medium consists essentially of 20 to 35 percent atoms of argon and 80 to 65 percent atoms of a xenon-based composition.

7. The invention of claim 6 wherein the xenon-based composition consists essentially of about 95 to 100 percent atoms of xenon and about 5 to 0 percent atoms of another selected component.

8. The invention of claim 7 wherein the other component is a member selected from neon, krypton, nitrogen, helium, and mercury.

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